[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Steric Effects in Displacement Reactions. X. A Convenient Calorimeter for Gas–Liquid Reactions. The Heats of Reaction of Trimethylboron with Pyridine and the Monoalkylpyridines[1]

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A calorimeter has been developed which can be used in connection with the high vacuum equipment for measuring the heats of reaction of gases, such as diborane and trimethylboron, with liquid reactants or solutions. A precision of 1% can be realized easily with relatively simple procedures and equipment. The heat of reaction of gaseous boron trifluoride with pyridine in nitrobenzene solution was determined to be 32.87 ± 0.16 kcal./mole. The heat of reaction of gaseous boron trifluoride with tetrahydropyran under the same conditions was 20.75 ± 0.17 kcal./mole. The difference between these values, 12.12 kcal./mole, represents the heat of reaction of pyridine with tetrahydropyran-boron trifluoride, both in nitrobenzene solution. This value agrees with the 12.19 kcal./mole value previously obtained by direct measurement in the mercury well calorimeter. The gas–liquid calorimeter was applied to the determination of the heats of reaction of gaseous trimethylboron with the pyridine bases in nitrobenzene solution. The heat of reaction ($-\Delta H$) with pyridine is 21.36 ± 0.17 kcal./mole: $(CH_3)_3B(g) + Py(soln.) = Py{:}B(CH_3)_3(soln.)$. It increases to 21.69 ± 0.09 for 3-picoline, and to 21.98 ± 0.18 to 4-picoline. The reaction with the 2-alkylpyridines did not go to completion. Equilibrium constants were determined for these reactions and the measured reaction heats were corrected for the calculated extent of the reaction. Including the estimated uncertainties in the correction, the heats of reaction are 16.1 ± 0.25 kcal./mole for 2-picoline, 15.1 ± 0.6 kcal./mole for 2-ethylpyridine and 13.7 ± 1.0 kcal./mole for 2-isopropylpyridine. Neither 2-*t*-butylpyridine nor 2,6-lutidine reacts with trimethylboron. From the difference in the heats of reaction of trimethylboron with 4- and 2-picoline, a strain of 5.9 kcal./mole is estimated for homomorphs of *o*-*t*-butyltoluene. The heat of solution of trimethylboron in nitrobenzene is 6.09 ± 0.08 kcal./mole. With the aid of this value, a heat of reaction of 15.27 ± 0.25 kcal./mole is calculated for the reaction $(CH_3)_3B(soln.) + Py(soln.) = Py{:}B(CH_3)_3(soln.)$. This compares with the value of 17.0 kcal./mole measured for the reaction with all components gaseous.

In pursuing our objective of comparing the strains in the transition states for typical displacement reactions with those of related molecular addition compounds, it became necessary to determine the heats of formation of the addition compounds of borane and trimethylboron with the alkyl substituted pyridine bases.[3] It appeared that the desired information could be obtained most simply by measuring the heats of reaction of diborane and trimethylboron with the pyridine bases.

Unfortunately, these Lewis acids are highly sensitive to oxygen and water and are, therefore, very difficult to handle by conventional calorimetric methods. Since they are easily handled in high vacuum equipment,[4] we undertook to develop a calorimeter that could be used in conjunction with such equipment and methods.

It was evident that the research program would require the measurement of the heats of a relatively large number of reactions. It appeared necessary, therefore, to sacrifice some precision for ease of operation. In particular, the tremendous difficulties involved in attempting to prepare and work with materials such as diborane and trimethylboron in purities as high as 99% led us to adopt as our goal a precision of 1%.

The calorimeter which was developed was tested by measuring the heat of reaction of hydrogen chloride with aqueous sodium hydroxide and of boron trifluoride with pyridine and with tetrahydropyran, both in nitrobenzene solution. It was then applied to the determination of the heats of reaction of trimethylboron with pyridine and the alkyl substituted pyridine bases.

Results

The Calorimeter.—In general, calorimeters are based on a glass Dewar vessel, or they are constructed of an all-metal reaction chamber. The first has the advantage that conduction and radiation losses can be minimized by a highly evacuated and silvered vacuum jacket. It suffers from the disadvantages of a large thermal lag, because of the low conductivity of the glass, and a high heat capacity, because of the thickness of glass required to withstand evacuation. On the other hand, metal calorimeters can be made with low heat capacity, but heat losses due to conduction and convection are large unless elaborate precautions are taken.[5]

It appeared that the advantages of both types of calorimeters could be achieved without their disadvantages by constructing a glass Dewar-type calorimeter with an inner metallic chamber connected to the vessel by metal to glass seals. Such a calorimeter was constructed using a thin platinum reaction chamber (Fig. 1). It proved highly effective with low heat losses through conduction and radiation, low heat capacity for the reaction chamber, and rapid establishment of thermal equilibrium.

In operation the liquid reactant (water, aqueous sodium hydroxide or pyridine base in nitrobenzene) is introduced by a pipet into the reaction chamber filled with nitrogen. With air in the outer jacket, temperature equilibration with the constant temperature bath is rapidly achieved. The jacket is now evacuated (to 10^{-5} mm.) and stirring initiated. The gaseous reactant, measured as a gas in a calibrated volume, is now permitted to pass under its own pressure through the sintered glass disk covered with mercury, an effective one-way valve. The temperature rise is followed on the calorimetric thermometer (graduated in 0.01°).

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(1) Based upon a thesis sumbitted by Daniel Gintis in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Research assistant at Purdue University, 1951–1952, on a con tract supported by the Atomic Energy Commission.

(3) H. C. Brown, D. Gintis and H. Podall, THIS JOURNAL, **78**, 5376 (1956).

(4) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(5) W. P. White, "The Modern Calorimeter," Chemical Catalog Co., (Reinhold Publ. Corp.), New York, N. Y., 1928.

Two calorimeters were used. They were calibrated against the heat of solution of hydrogen chloride in water.[6] The heat capacities of the two calorimeters were 4.16 ± 0.14 cal./deg. (7 determinations) and 4.52 ± 0.13 cal./deg. (6 determinations). The reproducibility was therefore within 0.2 cal. in a total heat capacity of 44 cal., considerably better than our 1% goal.

The rate of heat loss of these calorimeters was 0.004°/min. for a 1° thermal head. This small heat loss served to reduce the uncertainty in calculating the temperature rise from the reaction. Accordingly, it appears that this construction possesses real advantages.

The accuracy of the instrument was tested by measuring the heat of reaction of hydrogen chloride with aqueous sodium hydroxide. The difference in the heats of these two reactions is the heat of reaction of hydrochloric acid and sodium hydroxide. Accurate thermochemical data for this reaction are available from the study by Richards and Rowe.[7]

A total of six determinations gave the value 13.34 ± 0.07 kcal./mole for the heat of this reaction at 25°. The value obtained by correcting the data of Richards and Rowe to the same concentration and 25° was 13.44 kcal./mole. On this basis it was concluded that the results obtained with this calorimeter could be relied upon to within the desired accuracy.

The instrument was further tested by examining the heat of reaction of boron trifluoride with pyridine and with tetrahydropyran in nitrobenzene solution. The difference in the heats of these two reactions should correspond to the heat of reaction of pyridine with tetrahydropyran–pyridine, a reaction which had previously been measured by more conventional methods.[8]

$$BF_3(g) + Py(soln.) = Py{:}BF_3 \qquad \Delta H_1$$

$$BF_3(g) + THP(soln.) = THP{:}BF_3(soln.) \qquad \Delta H_2$$

$$Py(soln.) + THP{:}BF_3(soln.) = Py{:}BF_3(soln.) + THP(soln.)$$

$$\Delta H_1 - \Delta H_2 = \Delta H_3 \qquad \Delta H_3 = -12.19 \pm 0.08$$

The experimental data are summarized in Table I.

TABLE I

HEATS OF REACTION OF BORON TRIFLUORIDE WITH PYRIDINE AND WITH TETRAHYDROPYRAN IN NITROBENZENE SOLUTION AT 25°

Run	$BF_3(g) + Py(soln.)$ $(-\Delta H)$, kcal./mole	Run	$BF_3(g) + THP(soln.)$ $(-\Delta H)$, kcal./mole
1	33.28	1	20.65
2	33.00	2	20.54
3	32.77	3	21.13
4	32.96	4	20.63
5	32.75	5	20.80
6	32.56		
7	32.89		
8	32.76		
Mean	32.87 ± 0.16	Mean	20.75 ± 0.17

The difference between these two values ($\Delta H_1 - \Delta H_2$) is −12.12 kcal./mole as compared with the directly measured value of −12.19 kcal./mole.[8]

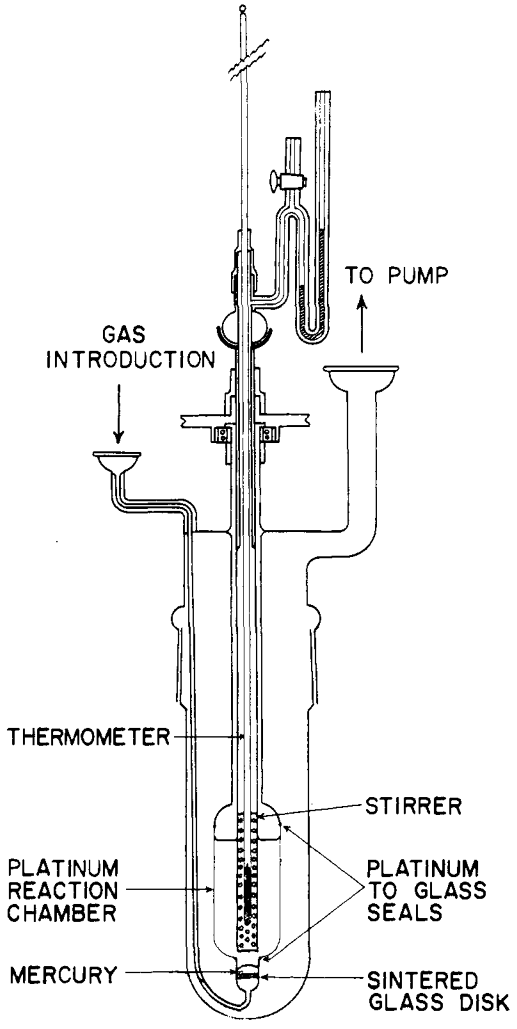

Fig. 1.—Gas–liquid calorimeter for use with high vacuum apparatus.

In previous papers we have reported the heats of reaction of tetrahydropyran–boron trifluoride with a number of pyridine bases.[8] For convenience in discussing the results the data were based on the reaction $BF_3(soln.) + Py(soln.) = Py{:}BF_3(soln.)$, using the value 25.0 ± 0.6 kcal./mole[8] in converting the results to this basis. In view of the fact that the reaction $BF_3(g) + Py(soln.) = Py{:}BF_3(soln.)$, is now known with much higher precision as a result of the present study, it has appeared desirable to revise the earlier treatment and to base the heats upon this reaction.[9]

Heats of Reaction of Trimethylboron.—The heats of reaction of trimethylboron with pyridine and the picolines, with all components gaseous, were investigated previously by examining the variation of the equilibrium constants with temperature.[10] Values of 17.0 and 17.8 kcal./mole were obtained for pyridine and 3-picoline.

Some difficulty was experienced with these derivatives because of the relatively low volatility of the addition compounds. These difficulties were mag-

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(6) W. A. Roth, *Z. Elektrochem.*, **50**, 107 (1944).

(7) T. W. Richards and A. W. Rowe, THIS JOURNAL, **42**, 1621 (1920); **43**, 771 (1921); **51**, 707 (1929).

(8) H. C. Brown and R. H. Horowitz, *ibid.*, **77**, 1730 (1955).

(9) See Table III, ref. 3.

(10) H. C. Brown and G. K. Barbaras, THIS JOURNAL, **69**, 1137 (1947).

nified for the 4-picoline derivative and it was believed that the experimental value of 19.4 kcal./mole was subject to a fairly large uncertainty. In the case of 2-picoline–trimethylboron the addition compound proved to be completely dissociated in the vapor phase and no thermodynamic data could be obtained. It therefore appeared that a study of the heats of reaction of trimethylboron with pyridine and the picolines should provide a rigorous test of the utility of the calorimetric technique. The success of this study led us to determine also the heats of reaction of trimethylboron with 2-ethyl- and 2-isopropylpyridine. No reaction was observed with 2-*t*-butylpyridine and 2,6-lutidine.

Measured quantities of trimethylboron were introduced into solutions of pyridine, 3-picoline and 4-picoline in nitrobenzene. The latter solutions were approximately 0.3 *M* in the base, representing a considerable excess over the trimethylboron introduced. The calorimeter was fitted with a manometer and the completeness of the reaction was established by following the pressure above the reaction solution in the calorimeter.

The results are summarized in Table II.

TABLE II

CALORIMETRIC HEATS OF REACTION OF TRIMETHYLBORON WITH PYRIDINE, 3-PICOLINE AND 4-PICOLINE IN NITROBENZENE SOLUTION AT 25°

Base	Trimethylboron, mmoles	ΔT, °C.	Molar heat of reaction $(-\Delta H)^a$ $(CH_3)_3B$ (g.)	$(CH_3)_3B$ (soln.)^c
Pyridine	0.919^d			
	2.698^b	2.671	21.48	
	0.312^d			
	2.806^e	2.735	21.14	
	2.778^e	2.730	21.36	
	2.813^e	2.742	21.25	
	2.738	2.731	21.59	
		Mean	21.36 ± 0.17	15.27
3-Picoline	0.894^d			
	2.664^e	2.680	21.82	
	2.768^e	2.742	21.55	
	2.717^e	2.694	21.63	
	0.655^d			
	2.404^f	2.414	21.78	
	2.934^f	2.923	21.67	
		Mean	21.69 ± 0.09	15.60
4-Picoline	0.274^d			
	2.781^e	2.855	22.27	
	2.771^e	2.828	22.20	
	2.769^e	2.747	21.63	
	0.548^d			
	2.664^f	2.702	22.01	
	2.540^f	2.553	21.78	
	2.684^f	2.707	21.99	
		Mean	21.98 ± 0.18	15.89

[a] Kcal./mole. [b] $-\Delta H$ for reaction: $(CH_3)_3B(g.) + Py(soln.) = Py{:}B(CH_3)_3(soln.)$. [c] $-\Delta H$ for reaction: $(CH_3)_3B(soln.) + Py(soln.) = Py{:}B(CH_3)_3(soln.)$. [d] Prerun to remove trace impurities. [e] Successive measurements on same solution. [f] Successive measurements on same solution.

The heat of solution of trimethylboron was also determined calorimetrically. The results are summarized in Table III.

TABLE III

MOLAR HEAT OF SOLUTION OF TRIMETHYLBORON IN NITROBENZENE AT 25°

Trimethylboron, m moles Introduced	In soln.^{a}	ΔT, °C.	Molar heat of solution $(-\Delta H)$, kcal./mole
2.626	2.219	0.624	6.12
2.702	2.285	.649	6.18
2.364	1.981	.543	5.96
		Mean	6.09 ± 0.08

[a] Corrected for trimethylboron in vapor phase of calorimeter. See Experimental part.

Using the value for the molar heat of solution, 6.09 kcal./mole, the heats of the reaction $(CH_3)_3B(soln.) + Py(soln.) = Py{:}B(CH_3)_3(soln.)$ have been calculated and are listed in Table II.

An attempt was made to measure the heat of reaction of trimethylboron with 2-picoline in the same manner as that used for pyridine and 3- and 4-picoline. However, it was observed that the measured heat of reaction increased with increasing concentration of the base in nitrobenzene. Thus the measured heat of reaction increased from 15.1 kcal./mole for 0.267 *M* 2-picoline, to 15.4 for 0.383 *M*, to 15.9 for 0.601 *M* solution. Evidently the reaction was not proceeding to completion.

The situation was even less satisfactory in the case of 2-ethylpyridine and 2-isopropylpyridine.

In the case of 2-*t*-butylpyridine and 2,6-lutidine the measured heats of "reaction" were 6.10 and 6.25 kcal./mole, respectively. These values are essentially identical with the 6.09 kcal./mole value obtained for the heat of solution of trimethylboron in nitrobenzene (Table III). Consequently, it appears that no reaction occurs between trimethylboron and these two bases.[11]

Even though no reaction occurs between 2-*t*-butylpyridine or 2,6-lutidine and trimethylboron, it was observed that the solubility of trimethylboron in the nitrobenzene solution of these bases was greater than in nitrobenzene itself.

The experimental results are summarized in Table IV.

TABLE IV

CALORIMETRIC HEATS OF REACTION OF TRIMETHYLBORON WITH 2-ALKYLPYRIDINES AND 2,6-LUTIDINE IN NITROBENZENE SOLUTION AT 25°

Base	Concn., *M*	Trimethylboron, mmoles	ΔT, °C.	Heat of reacn. per mole trimethylboron(g) Obsd.	Corr.^{b}
2-Picoline	0.267	0.547^a			
		2.586	1.727	15.06	15.87
	.267	0.505^a			
		2.650	1.758	14.97	16.09
	.383	0.550^a			
		2.525	1.755	15.44	16.06
	.604	0.319^a			
		2.474	1.795	15.84	16.15
	.604	2.615	1.921	15.90	16.01
2-Ethylpyridine	.534	2.448	1.439	13.19	14.79
	.534	2.386	1.417	13.60	15.04
2-Isopropylpyridine	.382	2.471	1.004	9.81	13.46
	.382	2.797	1.052	10.30	13.01
2-*t*-Butylpyridine	.278	2.111^c	0.593	6.10	
2,6-Lutidine	.278	2.296^c	0.660	6.25	

[a] Prerun to remove trace impurities. [b] Values corrected for incompleteness of reaction. [c] In solution.

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(11) H. C. Brown and R. B. Johannesen, THIS JOURNAL, **75**, 16 (1953).

It was clearly necessary to correct the thermal data for the reactions of trimethylboron with 2-methyl-, 2-ethyl- and 2-isopropylpyridine for the incompleteness of the reactions. The correction was made in the following manner. The pressures of trimethylboron above the solutions in the calorimeter were noted. These pressures in conjunction with the solubility of trimethylboron in nitrobenzene were used to calculate the amount of free trimethylboron in solution. From these data the amounts of combined trimethylboron could be directly estimated and the heats of reaction per mole of *combined* trimethylboron calculated.

It was observed that the solubility of trimethylboron in nitrobenzene containing 2-*t*-butylpyridine or 2,6-lutidine was somewhat greater than the solubility of trimethylboron in nitrobenzene itself. Since the reaction mixtures contain considerable free base, we considered the possibility that the solubility of trimethylboron in the reaction solutions might be better given by the solubility in these solutions rather than in pure nitrobenzene. Accordingly, we calculated the heats of reaction on this basis also.

The results of the two calculations are summarized in Table V.

TABLE V

THERMODYNAMIC DATA FOR THE REACTIONS OF TRIMETHYLBORON WITH THE 1-ALKYLPYRIDINES IN NITROBENZENE SOLUTION AT 25°[c]

Base	10^2K	$-\Delta F$, kcal./mole	$-\Delta H$, kcal./mole	$-\Delta S$, e.u.
2-Picoline[a]	1.00	2.76	15.1	22.3
2-Ethylpyridine[a]	4.36	1.85	13.2	17.5
2-Isopropylpyridine[a]	7.61	1.53	10.1	8.2
2-Picoline[b]	3.64	1.97	16.1	25.8
2-Ethylpyridine[b]	14.8	1.13	15.1	26.3
2-Isopropylpyridine[b]	38.2	0.41	13.7	24.3

[a] Concentration of free trimethylboron in solution calculated from solubility of gas in nitrobenzene. [b] Concentration of free trimethylboron in solution calculated from solubility of trimethylboron in nitrobenzene solutions of 2-*t*-butylpyridine and 2,6-lutidine. [c] The data are an average of a number of runs for each compound, several of which are reported in Table IV.

In the gas phase, addition compounds of the type under consideration exhibit entropies of dissociation in the neighborhood of 45 e.u.[10] These values do not vary significantly with changes in the structure of the amine. In solution a relatively constant value of approximately 24 e.u. would be expected for the entropy of dissociation for the trimethylboron addition compounds of the three bases. (Since the reaction is A + B = A:B, the entropy of the solution reaction will differ from that of the gas phase value by the entropy of vaporization of one mole of reactant.)

The data corrected on the basis of the solubility of trimethylboron in pure nitrobenzene show a marked variation in the entropy of dissociation, from 22.3 for 2-picoline-trimethylboron to 8.2 for 2-isopropylpyridine-trimethylboron. On the other hand, the values calculated on the assumption of the higher solubility of trimethylboron in the solutions exhibit a sensibly constant ΔS term of 24–26 e.u. For this reason we have adopted the latter values for the corrected heats of reaction.

In view of the relatively large uncertainties in this treatment, the heats of reaction of trimethylboron with 2-ethyl- and 2-isopropylboron must be assigned a much larger uncertainty than in the case of the other reactions here studied. If in addition to the estimated uncertainty of approximately ±0.2 kcal./mole in the experimental calorimetric heats, we assign an uncertainty of approximately 25% to the estimated corrections, the ΔH values become 16.1 ± 0.25 kcal./mole for 2-picoline, 15.1 ± 0.6 kcal. for 2-ethyl-, and 13.7 ± 1.0 kcal./mole for 2-isopropylpyridine.

Discussion

The experimental results are summarized in Table VI.

TABLE VI

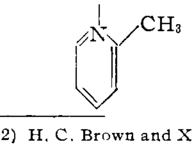
MOLAR HEATS OF REACTION OF TRIMETHYLBORON WITH PYRIDINE AND THE MONOALKYLPYRIDINES IN NITROBENZENE SOLUTION AT 25°

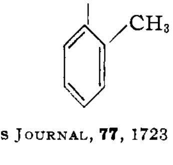
Base	Heat of reaction, kcal./mole, $-\Delta H$ $B(CH_3)_3$ (g)	$B(CH_3)_3$ (soln.)	$\Delta H_{Py} - \Delta H_B$, kcal./mole	$\Delta H_{4\text{-Pic}} - \Delta H_B$, kcal./mole
Pyridine	21.4	15.3	0	
4-Picoline	22.0	15.9	0.6	
3-Picoline	21.7	15.6	.3	
2-Picoline	16.1	10.0		− 5.9
2-Ethylpyridine	15.1	9.0		− 6.9
2-Isopropylpyridine	13.7	7.6		− 8.3
2-*t*-Butylpyridine	≤ 6.1	≤ 0		≤ −15.9
2,6-Lutidine	≤ 6.2	≤ 0		

The heat of reaction of trimethylboron with pyridine, all components in solution, is 15.3 kcal./mole. This compares with the 17.0 kcal./mole for the same reaction with all components gaseous.[10] Consequently, it appears that the heats of reaction under the two sets of conditions differ by an amount which is relatively small, but sufficiently important to make direct comparison difficult between data obtained under the two different experimental conditions.

An increase in the heat of reaction of 0.3 kcal./mole is observed for 3-picoline over pyridine and a larger increase of 0.6 kcal./mole is observed for 4-picoline. This corresponds to their relative base strengths. The pK_a values are: pyridine, 5.17; 3-picoline, 5.68; 4-picoline, 6.02.[12]

The pK_a value for 2-picoline, 5.97, is quite close to that for 4-picoline, so that a heat of reaction similar to that for the latter compound would be predicted for 2-picoline in the absence of steric effects. The sharp decrease in the heat of reaction, −5.9 kcal./mole (Table VI), is attributed to steric strain resulting from the conflicting steric requirements of the trimethylboron group and the 2-methyl substituent. In accordance with the discussion previ-





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[12] H. C. Brown and X. R. Mihm, THIS JOURNAL, **77**, 1723 (1955).

ously presented, strains of this magnitude are predicted for all homomorphs of *o*-*t*-butyltoluene.[13]

The strains, estimated similarly, increase slightly to 6.9 kcal./mole for 2-ethylpyridine, and to 8.3 kcal./mole for 2-isopropylpyridine. In the case of 2-*t*-butylpyridine the strains are estimated to be much larger, equal or greater than 15.9 kcal./mole.

The marked difference in the strains resulting from the interaction of trimethylboron with the 2-ethyl or the 2-isopropyl groups, as compared with the 2-*t*-butyl group is attributed to the difference in their geometries. The 2-ethyl and 2-isopropyl groups can rotate in such a way as to minimize their steric interactions with the trimethylboron molecule, whereas the 2-*t*-butyl group possesses essentially spherical symmetry. As a result, its ability to reduce the strain by rotation is greatly limited.

The present approach permits only an estimate for the minimum strain in the non-existent compounds of trimethylboron with 2-*t*-butylpyridine and 2,6-lutidine. However, it will be shown later that the present data in conjunction with earlier data on the heats of reaction of boron trifluoride with the pyridine bases permit a reasonable estimate of the strains in these addition compounds and their homomorphs.[14]

Experimental Part

Materials.—Boron trifluoride was obtained from a commercial cylinder (Matheson), introduced into the vacuum apparatus, and it reacted with anisole to form the addition compound. Volatile impurities were removed. The boron trifluoride was regenerated by careful heating and fractionated through traps at −80 and −150°. The product was tensiometrically homogeneous with a vapor pressure of 295 mm. at −111.8°.

Hydrogen chloride was prepared by dehydrating concentrated hydrochloric acid with concentrated sulfuric acid. After fractionation to remove entrained water vapor and sulfuric acid, successive fractions exhibited a constant vapor pressure of 125 mm. at −111.8°.

Trimethylboron was prepared by the reaction of methylmagnesium iodide with boron trifluoride in *n*-butyl ether solution.[15] The crude product was converted to the trimethylamine addition compound, purified by fractional sublimation, and regenerated with hydrogen chloride. The resulting product was tensiometrically homogeneous, with a vapor pressure of 31 mm. at −80°. Treatment with an equal volume of trimethylamine indicated the presence of 0.4% of an inert impurity, possibly carbon dioxide. All experimental data have been corrected for this impurity.

Pyridine (Reilly) was distilled in a column of 70 theoretical plates (b.p. 114.2° at 745 mm.). The purity was 99.8 mole % as indicated by cooling curve data. The pyridine bases[16] were samples which were previously described. Tetrahydropyran (du Pont) was fractionated in the 70-plate column, followed by distillation from lithium aluminum hydride to remove traces of peroxides or active hydrogen compounds. The material used exhibited b.p. 85.5° at 740 mm. and n^{20}D 1.4207. Nitrobenzene (du Pont) was distilled and stored over calcium hydride. A freezing point determination indicated a purity of 99.5 mole %.

Solutions of pyridine and tetrahydropyran in nitrobenzene were prepared with the utmost precautions to minimize contact with oxygen and moisture. The solutions were dried by storing for 7 days over calcium hydride with regular shaking.

The Calorimeter.—The assembled gas–liquid isothermal calorimeter is shown in Fig. 1. The reaction chamber is constructed of platinum, 0.025 in. in thickness, and contains 40 ml. of solution. The body of the calorimeter is connected to the gas introduction system on one side and to the high vacuum system on the other through clamped ball and socket joints. At the bottom of the reaction chamber a sintered disk (medium porosity) supporting 1 ml. of mercury serves as a one-way valve for the introduction of the gaseous reactant. (The large ground joint in the body was introduced solely to facilitate the construction.)

The stirrer consists of a hollow Tru-Bore shaft rotating in its closely fitting sleeve. At the bottom of the shaft there is sealed a perforated platinum cylinder. The stirrer, supported by a bearing which rests on a rubber sleeve, is driven by a rubber belt operating on the aluminum pulley. At the upper end of the stirrer assembly there is a socket joint (for vacuum tightness) connected to the thermometer and manometer assembly.

The thermometer and manometer assembly fits inside the stirrer and is connected by a ball and socket joint which permits the stirrer to rotate while the thermometer remains stationary. A calorimetric thermometer (Brooklyn Thermometer Co.), graduated in 0.01° is used and is read to the nearest 0.001° with a conventional meniscus viewer. The thermometers were calibrated against a Leeds and Northrup platinum resistance thermometer which in turn was calibrated against primary standards. Differential thermometer readings have an accuracy of ±0.002°.

The manometer is constructed of 2-mm. capillary tubing. It contains a stopcock to permit the partial evacuation of the calorimeter chamber. An aluminum shim between the thermometer and the ball joint aids alignment of the thermometer.

The calorimeter body is silvered. It is submerged in a constant temperature bath controlled to ±0.01°.

The gas introduction system is shown in Fig. 2. It is an integral part of the high vacuum apparatus.[4] The purified gaseous reactant is transferred to the calibrated bulb B. With the mercury at the calibration mark D, the pressure on the manometer C is read to the nearest 0.05 mm. with a cathetometer. At the pressures of 100–150 mm., it was established that errors resulting from non-ideality of hydrogen chloride, boron trifluoride and trimethylboron were less than 0.1% and therefore negligible.

The gas is then condensed into the introduction bulb F. The gas is introduced into the calorimeter at the desired rate through ball joint H by replacing the liquid nitrogen-bath used to condense the gas with another bath at an appropriate temperature, determined empirically. After the run is complete, the residual gas is condensed back into standard bulb B and measured. The gas introduced is taken as the difference.

The procedure was tested by measuring hydrogen chloride volumetrically as described above, introducing the gas into water contained in the calorimeter, and then titrating the acid in the calorimeter. Five determinations gave a maximum deviation of 0.6% and an average deviation of 0.3% for the amounts of hydrogen chloride estimated by the two methods.

Procedure.—The calorimeter is fitted with the stirring assembly and the Tru-Bore sleeve is carefully lubricated with Dow-Corning XC-20 silicone-graphite compound. One ml. of mercury is added through a microburet to cover the sintered glass disk. The calorimeter is placed into the constant temperature bath and connected to the high vacuum apparatus through the two ball and socket joints, lubricated with Apiezon N. The driving belt is now attached to the pulley of the stirrer. In runs involving gases which are sensitive to moisture or oxygen, the calorimeter is flushed out with nitrogen introduced through stopcock G. The solution is now added to the reaction chamber through a pipet, the socket joint of the stirrer assembly is treated with the silicone–graphite lubricant, and the thermometer–manometer assembly is placed into position. If the situation warrants the precaution, the nitrogen is passed through the solution for several minutes to remove dissolved oxygen. The chamber is now evacuated to approximately 650 mm. and the manometer stopcock is closed.

When the temperature is within 0.1° of the bath temperature, the outer jacket is evacuated to 10^{-5} mm. and the stirrer is started. The temperature is read for several minutes to establish the slope of the curve. (With the small temperature differential and the efficient jacket a

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[13] H. C. Brown, G. K. Barbaras, H. L. Berneis, W. H. Bonner, R. B. Johannesen, M. Grayson and K. L. Nelson, THIS JOURNAL, **75**, 1 (1953).

[14] H. C. Brown, D. Gintis and L. Domash, *ibid.*, **78**, 5387 (1956).

[15] H. C. Brown, *ibid.*, **67**, 374 (1945).

[16] H. C. Brown and W. A. Murphey, *ibid.*, **73**, 3308 (1951); H. C. Brown and A. Cahn, *ibid.*, **77**, 1715 (1955).

short fore-run of but 4–5 min. was usually ample to establish the slope with high precision.)

Meanwhile the gas is measured in the standard bulb and transferred to the gas introduction bulb F. At 20 sec. before zero time the liquid nitrogen-bath is removed and replaced by a bath of appropriate temperature. Time–temperature data are recorded each minute. When the final slope is definitely established, the run is stopped and the unused gas is transferred back to the standard bulb and measured. The reactant in the reaction chamber was used in slight excess.

After a calibration or reaction run, the calorimeter is taken apart, the lubricant cleaned off, and the chamber washed thoroughly with acetone. It is then dried by drawing dried air into the calorimeter with an aspirator. The calorimeter and parts are stored in a dry air-box. With these precautions we encountered no difficulty in working with either boron trifluoride and trimethylboron, reported in the present study, or with diborane, as reported in the following paper.[17]

For runs in nitrobenzene solution a modified procedure was found to permit two or even three measurements with a single filling of the calorimeter and to eliminate errors arising from the presence of small amounts of more reactive impurities. The success of the method depends upon the fortunate circumstance that the difference between the heat capacity of the solvent, nitrobenzene, and the reactants and product, pyridine base and addition compound, appears to be relatively small. This permits the use of relatively concentrated solutions of pyridine (and its derivatives) in nitrobenzene so that two or three successive determinations can be made on the same solution.

A small pre-run is first made with a small quantity of gas, but without recording temperature data. Such a pre-run should remove reactive impurities which have a larger heat of reaction than that of the compound being measured. Thus, a 2.0 kcal. difference in the heats of reaction will allow the preferential reaction of over 90% of the impurity.

A run is now made in the usual manner. After it is complete, the thermometer assembly is lifted, relubricated in a stream of nitrogen, and replaced. Meanwhile, the bath temperature is lowered about 4° and air is introduced into the outer jacket to facilitate return of the calorimeter contents to the original temperature. After approximately 20 min., the jacket is evacuated and a second run is carried out on the same solution. In some cases a third determination is possible.

Identical results have been obtained in three successive runs of this kind with those in individual determinations. The procedure exhibited its utility in measurements with trimethylboron and with diborane.[17] In these cases the occasional presence of traces of oxygen or water resulted in high heats of reaction in the first of three successive determinations. A marked difference between the first determination and the later measurements clearly indicated the presence of these impurities and facilitated the accurate determination of the true reaction heats.

Heats of Solution of Trimethylboron in Nitrobenzene and Nitrobenzene Solutions.—A total of 40.00 ml. of nitrobenzene was introduced into the calorimeter and the trimethylboron added in small increments. The apparatus contained a free vapor space of 20.0 ml. The following data were observed: 65 mm., 0.436 mmole of trimethylboron; 102 mm., 0.668; 189 mm., 1.243; 229 mm., 1.538; 319 mm., 2.126. These data were plotted and the graph used to estimate the amounts of trimethylboron in nitrobenzene solutions from the pressures exhibited by these solutions.

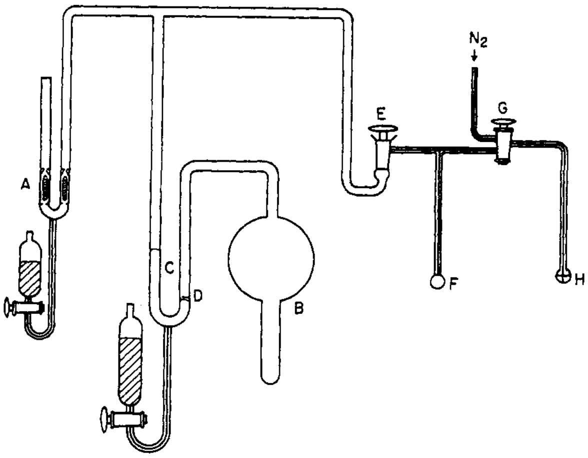

Fig. 2.—The gas introduction system.

The heat of solution of trimethylboron in nitrobenzene was determined in the following manner. A total of 40.00 ml. of nitrobenzene was introduced into the calorimeter and trimethylboron added. The temperature rise was followed in the usual manner. From the pressure in the calorimeter, the amount of trimethylboron in the nitrobenzene phase was calculated. In a typical experiment, of 2.626 mmoles of trimethylboron introduced, 0.407 mmole was in the gas phase and 2.219 mmoles estimated in solution. The temperature rise was 0.624°, resulting in a calculated heat of solution of 6.12 kcal./mole. Two additional determinations gave close agreement (Table III).

The heats of solution of trimethylboron in nitrobenzene solutions of 2,6-lutidine and 2-*t*-butylpyridine were determined in a similar manner (Table IV).

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[17] H. C. Brown and L. Domash, THIS JOURNAL, **78**, 5384 (1956).